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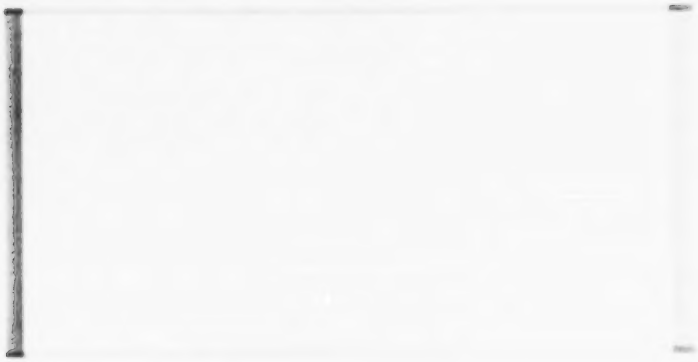

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A REVIEW OF THE INORGANIC AND ORGANOMETALLIC CHEMISTRY OF ZIRCONIUM

Report No 85-124-K

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ABSTRACT

The results of a literature review of the inorganic and organometallic chemistry of zirconium are presented. Compounds with physical and chemical properties compatible with the requirements of an ir laser zirconium isotope separation process have been identified.

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EXECUTIVE SUMMARY

A REVIEW OF THE INORGANIC AND ORGANOMETALLIC CHEMISTRY OF ZIRCONIUM

A. Kuksis Kalvins
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Chemical Research Department

This report presents the results of a literature review of the inorganic and organometallic chemistry of zirconium. The goal of the review was to identify candidate compounds for an infrared (ir) laser isotope separation process. In order for a compound to be suitable for ir laser based isotope separation it must have a stretching or bending vibration in its ir spectrum, ie, 9-16 μm (1111 - 625 cm^{-1}). The vibration must have an isotopic shift comparable with and preferably greater than its absorption width. The compound must also be relatively volatile at moderate temperatures, thermally robust and possess a relatively low activation energy to unimolecular decomposition or intramolecular reaction. A number of candidate compounds were identified, these include,

- anhydrous $ZrOCl_2$ (νZr-O 877 cm^{-1}, 11.5 μm)
- $[Zr(NR_2)_4]$ (νZr-N 533-677 cm^{-1}, 19-15 μm)
- $[Zr(SOCNR_2)_4]$ (νZr-O 552-569 cm^{-1}, 18-17.6 μm)
- $[Cp_2Zr(OR)_2]$ (νZr-O 1090-1140 cm^{-1}, 9.2-8.8 μm)
- $[Cp_xZr(NR_2)_{4-x}]$ (νZr-N 500-640 cm^{-1}, 20-15 μm).

Compounds such as $[Zr(hfacac)_4]$, $[Zr(tfacac)_4]$, $[Cp_2Zr(acac)_2Cl]$ and $[CpZr(hfacac)_3]$ (acac = acetylacetonate, hfacac = hexafluoroacetylacetonate, tfacac = trifluoracetylacetonate) may also be suitable however the data required to completely assess their potential, eg, ir spectra, are not available. The compounds $[ZrOCl_2]$, $[Zr(NEt_2)_4]$ and $[Zr(tfacac)_4]$ are commercially available.

Synthesis of many of these complexes involves a number of steps and yields are often low. All of the compounds should however be tested in order to assess the feasibility of ir laser based zirconium isotope separation. If the process is viable, methods to improve the yields can be examined.

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GLOSSARY OF ABBREVIATIONS

acac	acetylacetonate ion, 2,4-pentanedionate
as	asymmetric
n_{Bu}	n-butyl
cm^{-1}	wavenumber
C_p	π-cyclopentadienyl, η^5-C_5H_5
d^n	formal d-electron configuration
Et	ethyl
hfacac	hexafluoroacetylacetonate ion, 1,1,1,5,5,5-hexafluoro-2,4-pentanedionate
ir	infrared
L	any unidentate ligand
Me	methyl, CH_3
Ph	phenyl
n_{Pr}	n-propyl
R	an alkyl group
RT	room temperature
s,sym	symmetric
tfacac	trifluoroacetylacetonate ion, 1,1,1-trifluoro-2,4-pentanedionate
THF	tetrahydrofuran
X	a halogen
vs	very strong

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To Mr. F.J. Kee
Director of Research

A REVIEW OF THE INORGANIC AND ORGANOMETALLIC CHEMISTRY OF ZIRCONIUM

1.0 INTRODUCTION

The recent zirconium pressure tube cracking problems in Ontario Hydro's CANDU reactors have renewed interest in the development of a technique for removal of the zirconium-91 isotope from the zirconium isotope mix. Zirconium has five stable isotopes, see Table 1, the majority of which have a very low neutron absorption character. The zirconium-91 isotope however has a thermal neutron capture cross-section of 1.58 barns/1/. Selective removal of this isotope would permit construction and use of more conservative, ie, thicker zirconium pressure tubes without concomitant loss of fuel burn-up due to increased neutron absorption by the metal. Thicker pressure tubes would offer a number of advantages, these include

- increased resistance to hydride cracking,
- creep and elongation problems would be diminished,
- higher fuel channel temperature and pressure operating conditions could be accommodated resulting in a more efficient conversion of heat to power, ie, more power per kilogram of uranium/2/.

A possible route to zirconium isotope separation is one based on a uranium isotope separation technique using infrared lasers reported by Kaldor et al in 1979/3,4/. This method relies on increasing, in an isotopically selective fashion, the internal energy of a target molecule to the point where some thermally allowed intra- or intermolecular reaction, ie bond cleavage, proceeds at a suitable rate. In Kaldor's experiment, $[UO_2(hfacac)_2 \cdot THF]$ was irradiated with a CO_2 laser. The absorption band due to the asymmetric stretch of the moiety UO_2^{2+}, $\nu(O\text{-}U\text{-}O)$, falls within the range of the CO_2 laser. Irradiation at this frequency resulted in an isotope specific unimolecular dissociation of the molecule. The U-O bond associated with the THF ligand was broken, ie, the weakest bond in the molecule, resulting in loss of THF.

TABLE 1

STABLE ISOTOPES OF ZIRCONIUM/1/

Isotope	% Natural Abundance	Atomic Mass	Neutron-Capture Cross-Section (barns)
$_{40}Zr^{90}$	51.4	89.9043	0.10 ± 0.076
$_{40}Zr^{91}$	11.2	90.9053	1.58 ± 0.12
$_{40}Zr^{92}$	17.1	91.9046	0.25 ± 0.12
$_{40}Zr^{94}$	17.5	93.9061	0.075 ± 0.008
$_{40}Zr^{96}$	2.8	95.9082	0.05 ± 0.01

Application of infrared (ir) laser based isotope separation to removal of the zirconium-91 isotope requires an inorganic or organozirconium complex which contains a zirconium-91-ligand vibration within the operating range of an infrared laser. The purpose of this study was to examine the chemistry of zirconium in order to determine if there are any zirconium complexes, either commercially available or readily synthesized, which possess properties suitable for laser based zirconium isotope separation. In the following, the physical and chemical properties that a compound must possess to be suitable for laser based isotope separation, and the inorganic and organometallic chemistry of zirconium as related to these requirements are examined.

2.0 REQUIREMENTS

To be suitable for infrared laser based isotope separation, a complex must have a stretching or bending vibration in its ir spectrum at a frequency within the operating range of an infrared laser, ie, 9-16 μm (1111-625 cm^{-1}). The band must be relatively sharp, ie, $\leq$10 cm^{-1} fwhm, and in a region free of other absorptions/6/. The vibration must also have an isotopic shift comparable with and preferably greater than its absorption width.

The compound must be relatively volatile at moderate temperatures (~1 torr at 100°C), thermally robust and possess a relatively low activation energy to unimolecular decomposition or intramolecular reaction/3/. The molecule should be polyatomic in order that there is an abundance of vibrational-rotational transitions which may facilitate ready absorption of many photons up to the dissociation limit/5/. There is no such multiple absorption of ir photons in simple (two or three atom) molecules where the number of possible vibrational-rotational transitions is limited.

3.0 CHEMICAL AND PHYSICAL PROPERTIES OF ZIRCONIUM

Zirconium is a hard, corrosion resistant, high melting metal (mp 1855°C ± 15°C), resembling stainless steel in appearance/7/. An oxide film on the surface is believed to account for its lack of reactivity at room temperature. At higher temperatures zirconium is slowly attacked by aqua regia (HCl/HNO_3), phosphoric acid, hydrofluoric acid, sulphuric acid and molten sodium bisulphate, sodium carbonate and sodium peroxide. At higher temperatures it also reacts readily with hydrogen (reversibly), oxygen, nitrogen and the halogens.

Zirconium and hafnium occur together in nature and their chemistries are very similar. Unless specifically purified, zirconium usually contains from 0.5-2% hafnium/8/. Pure zirconium is required for nuclear applications and is prepared commercially via the Kroll process. The Kroll process involves reaction of the vapour of $ZrCl_4$ with molten magnesium under an atmosphere of pure helium or argon, Equation 1.

$$ZrCl_4(g) + 2\ Mg(\ell) \rightarrow 2\ MgCl_2(\ell) + Zr(s) \qquad (1)$$

The reaction is exothermic, $\Delta H^0_{1150\ K} = -78.6$ kcal/8/. Distillation at 925 K in vacuo removes the magnesium chloride and excess magnesium leaving a highly reactive zirconium sponge which is cooled under helium and compacted by arc melting under argon. Extremely pure zirconium is obtained by zone refining.

The most commonly observed oxidation states and stereochemistries of zirconium are summarized in Table 2. Zirconium in its elemental form has an electronic configuration with four valence electrons outside a noble gas core, ie $[Ar]5s^2 4d^2$. The chemistry of zirconium is restricted primarily to the reactions of the metal in the 4+ oxidation state. The zirconium 4+ ion is relatively large, spherical and highly charged. The high size to charge ratio of the Zr^{4+} ion renders it a relatively hard Lewis acid and thus promotes strong bond formation to small, (nonpolarizable) anions such as oxide or fluoride. The Zr^{4+} ion

TABLE 2

OXIDATION STATES AND STEREOCHEMISTRY OF ZIRCONIUM/7/

Oxidation State	Coordination Number	Geometry	Examples
Zr(0)	6	Octahedral (?)	$[Zr(bipy)_3]$(?)
Zr(I) d^3 Zr(II) d^2		Complex sheet and cluster structures	
Zr(III) d^1	6	Octahedral	$ZrCl_3$, $ZrBr_3$, ZrI_3
Zr(IV) d^0	4	Tetrahedral	$ZrCl_4(g)$, $Zr(CH_2C_6H_5)_4$
	6	Octahedral	Li_2ZrF_6, $Zr(acac)_2Cl_2$ $ZrCl_6^{2-}$, $ZrCl_4(S)$
	7	Pentagonal bipyramidal	Na_3ZrF_7, $K_2CuZr_2F_{12}\cdot 6H_2O$
		Capped trigonal prism	$(NH_4)_3ZrF_7$
		Tetragonal base-trigonal base polyhedron	ZrO_2
	8	Square antiprism Dodecahedron	$Zr(acac)_4$, $Zr(SO_4)_2\cdot 4H_2O$ $[Zr(C_2O_4]_4^{4-}$, $]ZrX_4(diars)_2]$ $[Zr_4(OH)_8(H_2O)_{16}]^{8+}$

has no partly filled outer electron shell to give it stereochemical preferences. These properties result in high coordination numbers, eg 6, 7, 8, and a great variety of coordination polyhedra. Discrete, 4-coordinated molecular species are found only in special cases, generally when there is steric hindrance combined with ligand-donor π-bonding, eg $Zr(BH_4)_4$, $Zr(allyl)_4$, $Zr(NR_2)_4$. In general, the most common higher coordination number is eight. This is usually promoted by the most electronegative donors, F^-, O^{2-}, OH^-, OH_2 or by polydentate groups.

The following review of the chemistry of zirconium is divided into two parts, inorganic and organometallic complexes. Organometallic compounds are those in which the carbon atoms of organic groups are bound to metal atoms/7/. The term inorganic compound denotes all other complexes, ie, those containing metal-halogen, metal-oxygen, metal-nitrogen bonds, etc.

3.1 Inorganic Chemistry

Inorganic complexes of zirconium include zirconium halides, oxides, chalcogenides, phosphates, etc. Zirconium halides, specifically $ZrCl_4$, are common starting materials for the preparation of many other inorganic and organometallic zirconium complexes and will be discussed first.

All four zirconium tetrahalides, ZrF_4, $ZrCl_4$, $ZrBr_4$ and ZrI_4 are known and are commercially available/9/. The compounds are tetrahedral monomers in the gas phase and the solids are polymers with bridging halides. The infrared stretching frequencies of Zr-X generally occur at frequencies too low for an infrared laser, eg.

νZr-Cl (terminal, gas) = 431-388 cm^{-1} (23-26 μm);
νZr-Cl (bridge, solid) = 310-291 cm^{-1} (32-34 μm) /8/.

These compounds are therefore not expected to be suitable candidates for an ir laser zirconium isotope separation process. Derivatives of some of the tetrahalides may however be useful.

Zirconium tetrachloride is a white, crystalline polymeric solid subliming at 331°C/7/. The polymer consists of zig-zag chains of $ZrCl_6$ octahedra. $ZrCl_4$ fumes in moist air and is vigorously hydrolyzed, Equation 2/7/.

$$ZrCl_4 + 9\ H_2O \rightarrow ZrOCl_2 \cdot 8H_2O + 2\ HCl \qquad (2)$$

The product of hydrolysis, $ZrOCl_2 \cdot 8H_2O$, is a stable oxide chloride containing the polymeric cation $[Zr_4(OH)_8(H_2O)_{16}]^{8+}$

together with chloride ions. Anhydrous $ZrOCl_2$ is made by reaction of chlorine monoxide and $ZrCl_4$. Its infrared spectrum is interpreted on the basis of an ionic aggregate of $[Zr=O]^{2+}$ and polymeric $[ZrOCl_4]^{2-}_n$. The ir spectrum shows a broad band at 877 cm^{-1} (11.5 μm) which is assigned to ν(Zr=O). There is however considerable doubt about the existence of a species such as $[Zr=O]^{2+}$/8/.

The chemistries of zirconium tetrabromide and zirconium tetraiodide are similar to zirconium tetrachloride. Zirconium tetrafluoride is a white solid which sublimes at 903°C/7/. It has an eight coordinate structure consisting of square antiprisms which are joined by sharing fluorines. The infrared spectrum of the vapour at 800°C shows bands at 668 cm^{-1} (15 μm) and 190 cm^{-1} (52.6 μm) due to Zr-F stretching and bending modes, respectively. The ir spectrum of the solid shows a Zr-F stretching band at 550 cm^{-1} (18.2 μm) and ZrF bending vibrations at 320, 295 and 255 cm^{-1} (31.3, 33.9 and 39.2 μm, respectively)/8/. ZrF_4 is the only tetrahalide which combines with H_2O to form stable hydrates, $ZrF_4 \cdot xH_2O$, x = 1 or 3. The trihydrate has an eight coordinate structure with two bridging fluorides, $(H_2O)_3F_3ZrF_2ZrF_3(H_2O)_3$ /7/.

The best known zirconium trihalides are $ZrCl_3$, $ZrBr_3$ and ZrI_3. The structures of these compounds consist of close-packed halide layers between which equally spaced zirconium atoms occupy one-third of the octahedral interstices to form infinite linear chains of metal atoms perpendicular to the layers, ie, infinite parallel chains of MX_6 octahedra sharing opposite faces/7/.

There is some evidence suggesting the existence of ZrX_x, $1 \leq x < 3$. The structure is believed to consist of stacked, hexagonally packed layers of either all metal atoms or all X atoms, with a stacking sequence XMMX...XMMX. The X...X interlayer distances are normal van der Waals contacts and the M-X distances are appropriate for single bonds/7/. The monohalides have great thermal stability (mp > 1100°C), metallic reflectivity, cleave like graphite and are generally metallic in character. ZrCl and ZrBr react with H_2 to give discrete though nonstoichiometric phases, eg $ZrXH_{0.5}$, ZrXH, X = Cl,Br. The hydrogen atoms are inserted through and between double metal layers of the initial halides/7/.

The main oxide formed by zirconium is ZrO_2. The material has an extremely high melting point, 2700°C, good mechanical properties and is exceptionally resistant to attack by both acids and alkalis/7/. The compound has a number of structures including the monoclinic form shown in Figure 1/8/. At very high temperatures a number of 'zirconates' may be prepared by reaction of ZrO_2 with metal oxides, metal hydroxides, etc.

A number of zirconium chalcogenides, ZrY_x, x = 3,2, Y = S,Se,Te, also exist. Zirconium exhibits a lower coordination number in ZrS_2 than in ZrO_2. The disulphide is stable in air or water, but is readily attacked by oxidizing reagents. The lower zirconium selenides and tellurides are similar to the corresponding sulphides. All compounds have layered structures and are intrinsic semiconductors/7/.

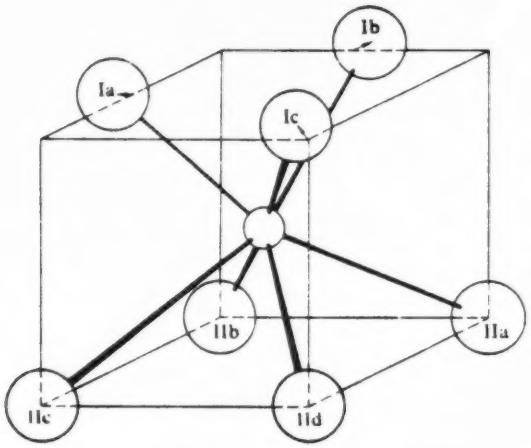


Figure 1. Monoclinic ZrO_2 (baddeleyite). Small circle = Zr atom; large circles = oxygen atoms./8/

Zirconium nitrides (ZrN), phosphides (ZrP_2, ZrP, Zr_3P), arsenides ($ZrAs_2$), carbides (ZrC), silicides ($ZrSi_2$, Zr_5Si_4, Zr_2Si), germanides and borides are also known. Most of these compounds have very high melting points, eg ZrN, mp 2980°C; ZrC, mp 3500°C; and complicated structures/8/.

$ZrCl_4$ is a common starting material for the preparation of a number of other inorganic zirconium complexes. Reaction of $ZrCl_4$ with carboxylic acid derivatives yields zirconium carboxylates, eg

$[Zr(O_2CR)_4]$
$[ZrO(O_2CR)_2(H_2O)_x]$
$[ZrO(OH)(O_2CR)(H_2O)_x]$.

As the alkyl chainlength is increased, solubility in water decreases and solubility in hydrocarbons increases. Some solution ir studies of zirconium carboxylates have been reported/10/. Bands in the 650 cm^{-1} (15.4 μm) and 470 cm^{-1} (21.3 μm) region were generally assigned to νZr-O. This region

of the ir spectra was not however well characterized. Thermal stability of the tetracarboxylates is not great and decomposition to oxycompounds occurs readily/8/. This thermal instability may preclude their utility in ir laser based Zr isotope separation. Recall from Section 2.0, one of the requirements was that the compound be thermally robust.

Tetrakis diketonates such as $Zr(acac)_4$, acac = acetylacetonate, are also known. $Zr(acac)_4$ is commercially available/9/. The crystal structure of $Zr(acac)_4$ reveals that it is eight-coordinate and the diketonate rings are slightly distorted/8/. The ir spectrum of these compounds is well characterized. The zirconium-oxygen stretching frequency is sensitive to the metal coordination number in the series $Zr(acac)_4$, $ZrCl(acac)_3$, $ZrCl_2(acac)_2$. The absorption band due to the Zr-O symmetric stretch generally occurs in the region 449-460 cm^{-1} (22.3-21.7 μm), the Zr-O asymmetric stretch in the region 421-450 cm^{-1} (23.8-22.2 μm) and νZr-X, X = halogen, in the region <314 cm^{-1} (>32 μm), see Table 3/8/.

Analogous hexafluoroacetylacetonate (hfacac) and trifluoroacetylacetonate (tfacac) zirconium complexes have also been prepared/11/. The fluorine containing derivatives are generally more volatile than the analogous acac compounds and melting points decrease in the series acac, tfacac, hfacac/11/. Infrared data have been reported for $Zr(hfacac)_4$ and $Zr(tfacac)_4$, however the region below ~1000 cm^{-1}, ie the region where ν(Zr-O) would be seen, was not well characterized/11/. In general the absorption bands in the fluorine substituted complexes are shifted to higher wavenumbers relative to those seen for the acac species. Therefore, although the Zr-O stretching vibrations for the acac derivative, $[Zr(acac)_4]$, are out of the range of an ir laser, νZr-O in the analogous fluorine substituted compound may fall within the operating range of an ir laser. Tetrakis(trifluoroacetylacetonate) zirconium is commercially available/9/.

A number of zirconium alkoxy compounds have also been reported. The tetraalkoxides are coordination polymers, $[M(OR)_4]_n$ (n ~ 3.5 for lower aliphatic R groups) due to bridging by alkoxide groups/8/. Steric hindrance in secondary and tertiary alkoxide groups prevents bridging and leads to volatile, monomeric compounds. The alkoxides are readily hydrolyzed and react with hydroxylic compounds, acids, β-diketonates, etc. The infrared spectra of these compounds have been well characterized, see Table 4. The Zr-O (bridging) stretching vibration generally falls in the region 400-600 cm^{-1} (17-23 μm). The polymeric nature of the compounds, ie low volatility, decreases their potential utility in an ir laser isotope separation process.

TABLE 3

INFRARED ABSORPTIONS OF SELECTED ZIRCONIUM DIKETONATE COMPLEXES/7/

Complex	$\nu(Zr\text{-}O)_s$ cm^{-1}	(μm)	$\nu(Zr\text{-}O)_{as}$ cm^{-1}	(μm)	$\nu(Zr\text{-}X)$ cm^{-1}	(μm)
$Zr(acac)_4$			421 301	(23.8) (33.2)		
$ZrCl(acac)_3$	449	(22.3)	432	(23.1)	314	(31.8)
$ZrBr(acac)_3$	449	(22.3)	434	(23.0)	164	(61)
$ZrI(acac)_3$	452	(22.1)	438	(22.8)	93	(108)
$ZrCl_2(acac)_2$	460	(21.7)	450	(22.2)	335 325	(30) (31)
$ZrBr_2(acac)_2$	460	(21.7)	450	(22.2)	213	(47)

acac = acetylacetonate ligand, $CH_3C(O)\,CH\,C(O)CH_3$

s = symmetric stretch
as = asymmetric stretch

Reaction of $ZrCl_4$ with N_2O_5 yields the adduct I, Equation 3/6/,

$$ZrCl_4 + (4+x+y)N_2O_5 \xrightarrow{30°C} \underset{I}{Zr(NO_3)_4 \cdot xN_2O_5 \cdot yN_2O_4} + 4NO_2Cl \quad (3)$$

The compound forms colourless sublimable crystals but decomposes at 140°C. The ir spectrum of I suggests that the nitrate groups are bidentate. The far ir and Raman spectra have been interpreted in terms of a tetrachelated, 8-coordinate (dodecahedral) molecule/8/. The Zr-O stretching vibrations were not however reported. A number of basic zirconium nitrates are known. These include $[Zr(OH)_2(NO_3)_2(H_2O)_4]$, $[ZrO(NO_3)_2]$, $[Zr(diket)_2(NO_3)_2]$, and $[Zr(NO_3)_4]$. Zirconium nitrate, in an aqueous solution, is commercially available/9/.

TABLE 4

PHYSICAL PROPERTIES OF SELECTED ZIRCONIUM ALKOXIDES/8/

Compound	Volatility (°C/mm Hg)	Degree of Polymerization	ΔH_{vap} (kcal $mole^{-1}$)	IR Spectra (νZr-O)	
				cm^{-1}	μm
$[Zr(OCH_3)_4]$	280/0.1	-	-	492, 430	20.3, 23.3
$[Zr(OC_2H_5)_4]$*	234.8/5.0	3.6	30.2	520, 463, 412	19.2, 21.6, 24.3
$[Zr(OC_3H_7)_4]$*					
$[Zr\{OCH(CH_3)_2\}_4]$**	203.8/5.0	3.57	31.5	567, 550, 510, 459	17.6, 18.2, 19,6, 21.8
$[Zr(OC(CH_3)_3)_4]$	89.1/5.0	1.0	15.2	557, 540	18.0, 18.5
$[Zr(OSi(CH_3)_3)_4]$	135/0.1	2.05	-	521	19.2
$[Zr(OC_4H_9)_4 \cdot C_4H_9OH]$*					

* commercially available/9/

**$[Zr(OC_3H_7)_4 \cdot C_3H_7OH]$ available from Alfa/9/

Zirconium amides of the type $[ZrX_4(NH_3)_x]$, X = Cl, Br, I, x = 8-10; $[ZrCl_4L_2]$, L = Me_3N, Et_3N, Me_2NH, Et_2NH; and $[Zr(NR_2)_4]$ have also been reported/8/. The zirconium-nitrogen vibration in the ir spectrum generally occurs in the 533-677 cm^{-1} (18.8-14.8 μm) region. Some examples of compounds, together with their ir data are listed in Table 5. The tetrakisdialkylamidozirconium complexes have a high reactivity with respect to protolytic substitutions and insertion reactions. The diethylamine derivative is available commercially/9/. The ir Zr-N stretching vibrations lie at the outside edge of the range of the ir laser and the compounds should be tested for their potential use in Zr isotope separation.

The best characterized zirconium phosphate is α-$Zr(HPO_4)_3 \cdot H_2O$. The complex has a unique crystal structure, sheets of Zr^{4+} are sandwiched between sheets of HPO_4^{2-}. Each Zr^{4+} is in an almost perfect octahedral set of oxygen atoms/8/. Between the sandwich layers are sheets of P-OH groups and water molecules. No ir data were reported.

Reaction of $ZrCl_4$ with tertiary phosphines yields dimeric zirconium complexes containing a zirconium-zirconium bond/12/.

$$ZrCl_4 + 2L \xrightarrow[Na/Hg]{\text{toluene}} 0.5\ [ZrCl_3L_2]_2 \qquad (4)$$

II

L = PMe_3, PEt_3, PPr_3, PBu_3

In solution II appears to exist in equilibrium with III, Equation 5.

$$Zr_2Cl_6L_4 \rightleftharpoons Zr_2Cl_6L_3 + L \qquad (5)$$

II III

No ir spectral data were reported/12/.

Reaction of zirconium tetrachloride with alkalithiocarbamates yields zirconium tetrathiocarbamates in high yields, Equation 6 /13/.

$$ZrCl_4 + 4\ Na(SOCNR_2) \longrightarrow [Zr(SOCNR_2)_4] + 4\ NaCl \qquad (6)$$

R = Me, Et

85 - 95% yields

TABLE 5

PHYSICAL PROPERTIES OF SELECTED DERIVATIVES OF $[Zr(NR_2)_4]$

R	mp (°C)	Volatility °C/mm Hg	νZr-N cm^{-1} (μm)	νNC_2 sym cm^{-1} (μm)
Me (CH_3)	70	60/0.001	537 s (18.6)	936 vs (10.7)
Et (C_2H_5)*	liquid	110/0.01	557 m (17.3)	1000 vs (10)
^{n}Pr(C_3H_7)	liquid	165/0.1	637 (15.7)	
^{n}Bu (C_4H_9)	liquid	180/0.1	637 (15.7)	

* available commercially from Alfa/9/

The thiocarbamate ligands are bidentate and the zirconium complexes are eight coordinate. The compounds are thermally stable, hydrolytically unstable, soluble in CH_2Cl_2, $CHCl_3$, but insoluble in saturated hydrocarbons. Solubility in water increases with the size of the alkyl group. The compounds are hydrolyzed rapidly upon exposure to air. Their ir spectra show strong bands in the 1500-1550 cm^{-1} (6.7-6.5 μm) region due to the C≡≡≡O and C≡≡≡N coupled stretching vibrations and bands in the range 552-569 cm^{-1} (18.1-17.6 μm) due to ν(Zr-O). No strong absorptions which can be attributed to ν(Zr-S) were observed in the region 250-380 cm^{-1} (40-26.3 μm). These bands may however be too weak to be observed/13/.

Tetrakis-N,N-dialkyldithiocarbamate zirconium compounds, $[Zr(S_2CNR_2)_4]$, have also been reported. Their ir spectra consist of bands in the region 1488-1520 cm^{-1} (6.7-6.6 μm) due to ν(N≡≡≡C), 994-998 cm^{-1} (~10 μm) due to ν(C-S) and ν(Zr-S) is found in the range 353-359 cm^{-1} (~28 μm). The dialkyldithiocarbamate ligand behaves as a chelate/8/.

A number of inorganic zirconium complexes have been reviewed in the previous section, however, only a very small fraction of these compounds appear to meet the requirements outlined in Section 2.0. Compounds which have an ir absorption band within or close to the range of an ir laser, 9-16 μm (1111-625 cm^{-1}), include

- anhydrous $ZrOCl_2$ (νZr-O 877 cm^{-1}, 11.5 μm)
- $[Zr(NR_2)_4]$ (νZr-N 533-677 cm^{-1}, 19-15 μm)
- $[Zr(SOCNR_2)_4]$ (νZr-O 552-569 cm^{-1}, 18-17.6 μm).

Zirconium diketonates such as $[Zr(acac)_4]$ are not suitable because their Zr-O stretching vibrations fall outside the range of an ir laser, ie in the region 440-460 cm^{-1} (22.7-21.7 μm). The Zr-O stretching vibrations of the analogous fluorine substituted compounds, eg $[Zr(hfacac)_4]$, are however expected to be shifted to higher wavenumbers relative to νZr-O for $[Zr(acac)_4]$. This shift might bring the νZr-O within the range of the ir laser. The zirconium-oxygen stretching and bending vibrations should be characterized for the fluorine substituted zirconium acetylacetonate complexes.

The Zr-O stretching bands in the ir spectra of zirconium carboxylates, eg $[Zr(O_2CR)_4]$, also lie close to the range of an ir laser, however the compounds are not thermally stable. If the problem of poor thermal stability could be overcome, ie with different alkyl groups (R), the compounds should be tested with an ir laser.

The compounds [$Zr(NEt_2)_4$] and [$Zr(tfacac)_4$] are commercially available/9/ and could quickly be prepared for testing with an ir laser.

3.2 Organometallic Chemistry

The designation organozirconium complex is given to a complex containing a direct zirconium to carbon link. Organozirconium compounds can be divided into four classes:

i) π-cyclopentadienyls and arenes,
ii) alkyls and aryls,
iii) allyls,
iv) carbonyls, nitrosyls and cyanides /7/.

All syntheses of organozirconium compounds must be carried out under dry, inert atmospheres, ie, under argon. Each class of compound will be reviewed briefly in the following section.

The most predominant organozirconium complexes are those which contain the cyclopentadienyl unit, $(\eta^5\text{-}C_5H_5)_2Zr$, eg Cp_2ZrHCl, where $Cp = \eta^5\text{-}C_5H_5$. The majority of cyclopentadienyl zirconium complexes are prepared from Cp_2ZrCl_2. The versatility of Cp_2ZrCl_2 as a starting material is illustrated in Figure 2. Cp_2ZrX_2, X = Cl,Br is prepared from zirconium tetrahalide and the cyclopentadienide Grignard reagent or alkali metal cyclopentadienide, Equations 7,8.

$$2(C_5H_5)MgBr + ZrBr_4 \rightarrow Cp_2ZrBr_2 + 2MgBr_2 \qquad (7)$$

30% yield

$$2NaC_5H_5 + ZrCl_4 \xrightarrow[\text{reflux}]{\text{THF}} Cp_2ZrCl_2 + 2NaCl \qquad (8)$$

81% yield

Cp_2ZrCl_2 has an essentially tetrahedral geometry. Its infrared spectrum is well characterized. The Zr-Cp stretching vibration occurs at 358 cm^{-1} (27.9 μm) and the Zr-Cl stretching vibration is found at 333 cm^{-1} (30 μm)/14/. Both stretching frequencies are considerably out of the range of the infrared lasers commercially available at present.

Cp_2ZrX_2 compounds containing halides other than chlorides are best prepared from the commercially available Cp_2ZrCl_2 via halide exchange reactions. Replacement of C_5H_5 by C_5H_4Me and C_5Me_5 enhances the solubility and crystallizability of $[(\eta^5\text{-}C_5H_5)_2\ ZrL_2]$ type complexes.

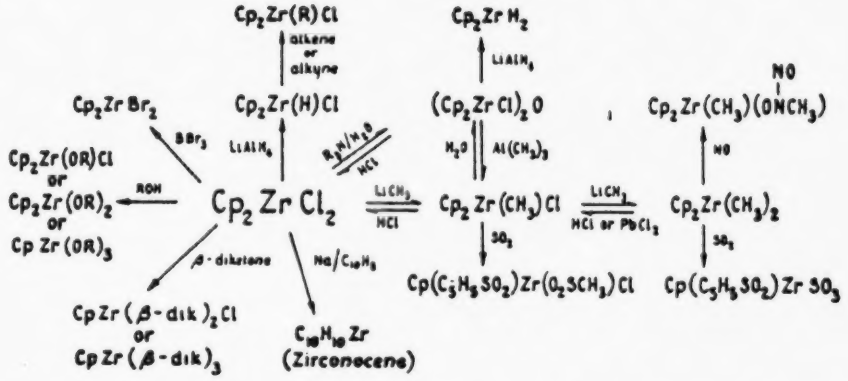


Figure 2. Reaction schemes for Cp_2ZrCl_2, demonstrating its utility as a starting material.

Cp_2ZrCl_2 is readily hydrolyzed in the presence of base to give $Cp_2Zr(Cl)OZr(Cl)Cp_2$, Equation 9 /14/.

$$2Cp_2ZrCl_2 + 2\,C_6H_5NH_2 + H_2O \xrightarrow[5\text{-}15\ min]{\text{room temp}} \underset{\text{IV}}{Cp_2Zr(Cl)-O-Zr(Cl)Cp_2} + 2C_6H_5NH_2\cdot HCl \qquad (9)$$

The product, IV, is colourless, sublimes at 200-220°C in vacuo and is stable in air and light for periods greater than one month. It is soluble in all common organic solvents except saturated hydrocarbons. The infrared spectrum shows an intense absorption band in the range 749-755 cm^{-1} (13.4-13.3 μm) due to the metal-oxygen-metal stretching vibration. The dimeric compound may not however be suitable for laser based isotope separation because of the complication of two zirconium atoms per molecule. The probability of the bimetallic complex having two Zr-91 atoms is very low, therefore the Zr-91 decomposition product may contain significant quantities of all other Zr isotopes. The yield of the Zr-91 depleted product would thereby be considerably reduced. Reaction of $[Cp_2ZrCl]_2O$ with protic reagents (HX) yields the monomer $Cp_2Zr(Cl)X$, Equation 10 /13/.

$$[Cp_2ZrCl]_2O + 2HX \rightarrow 2Cp_2Zr(Cl)X + H_2O \quad (10)$$

A number of Cp_2Zr complexes containing oxygen bonded organic ligands have also been synthesized. These include alkoxides, phenoxides, β-diketonates, carboxylates, sulfinates and sulfonates. To illustrate,

$$Cp_2ZrCl_2 + 2\ NaOC(CH_3)_3 \xrightarrow[Et_2O\ or\ C_6H_6]{RT} Cp_2Zr[OC(CH_3)_3]_2 + NaCl \quad (11)$$

86% yield

Bis(cyclopentadienyl)alkoxides and phenoxides, eg $[Cp_2Zr(OC_6H_5)_2]$, are white crystalline compounds readily soluble in most organic solvents. In contrast to the tetraalkoxide derivatives discussed in Section 3.1, these species are not polymers. The ir spectra of these compounds have been well characterized. The C-O stretching vibrations for the phenoxides are found in the 1280-1300 cm^{-1} (7.8-7.7 μm) region and in the 1090-1140 cm^{-1} (9.2-8.8 μm) range for alkoxides. Bands between 730-765 cm^{-1} (13.7-13.1 μm) have been tentatively assigned to Zr-O bending modes while those in the 420-570 cm^{-1} (23.8-17.5 μm) region were considered to arise from Zr-O stretching vibrations/14/. These infrared bending and stretching vibrations of the biscyclopentadienylzirconium alkoxides fall within or close to the operating range of ir lasers. The synthesis of these compounds however requires a number of steps and yields vary from 20 to 98%. The compounds may however be worth testing just to see if laser based isotope separation is possible.

Reaction of Cp_2ZrCl_2 with β-diketones (except the tri- or hexafluorinated derivatives) yields the bis(β-diketonate) complex V, Equation 12 /14/.

$$Cp_2ZrCl_2 + 2acacH \rightarrow Cp_2Zr(acac)_2Cl + HCl + C_5H_6 \quad (12)$$

V

94-98% yield

With either hexafluoro- or trifluoroacetylacetone the tris(diketonato) complex is obtained, Equation 13 /14/.

$$Cp_2ZrCl_2 + 3\ F_6\text{-}acacH \rightarrow CpZr(F_6\text{-}acac)_3 + C_5H_6 + 2HCl \quad (13)$$

Zirconium-oxygen infrared stretching frequencies have not been reported for the acac, hfacac nor tfacac derivatives.

Reaction of Cp_2ZrCl_2 with excess lithium borohydride yields $Cp_2Zr(BH_4)_2$. Treatment of $Cp_2Zr(BH_4)_2$ with a tertiary amine, eg trimethylamine yields the dihydride, Equation 14 /14/.

$$Cp_2Zr(BH_4)_2 + 2(CH_3)_3N \xrightarrow{C_6H_6} Cp_2ZrH_2 + 2(CH_3)_3NBH_3 \qquad (14)$$

Cp_2ZrH_2 is a polymer, nonvolatile and completely insoluble in all solvents. It is hydrolyzed only slowly in air. The zirconium-hydrogen stretching frequency occurs in the region 1300-1540 cm^{-1} (7.79-6.59 μm). The monohydride is similarly prepared, Equation 15 /14/.

$$Cp_2Zr(BH_4)_2 + (CH_3)_3N \xrightarrow{C_6H_6} Cp_2Zr(H)BH_4 + Me_3NBH_3 \qquad (15)$$

The monohydride, in contrast to the dihydride, is a monomer, air reactive, sublimes in vacuo at 60°C and is soluble in organic solvents. The zirconium-hydrogen stretching frequency occurs at 1945 cm^{-1} (5.1 μm). The Zr-H vibration is found at the other end of the working range of an ir laser, relative to νZr-O, νZr-N and νZr-Cl.

Reaction of Cp_2ZrCl_2 with allylmagnesium chloride yields the bisallyl complex, Equation 16 /14/.

$$Cp_2ZrCl_2 + 2\ C_3H_5MgCl \xrightarrow{0°C} Cp_2Zr(C_3H_5)_2 + 2\ MgCl_2 \qquad (16)$$

VI

VI is unstable and decomposes after several hours at room temperature in light. The C=C stretching vibrations in the ir spectra, 1533 cm^{-1} (6.5 μm) and 1589 cm^{-1} (6.3 μm), suggest that one allyl ligand is σ-bonded and the other π-bonded to the metal/15/.

Sulfur and selenium derivatives are prepared as shown in Equation 17,

$$Cp_2ZrCl_2 + HSC_6H_5 + 2N(CH_2CH_3)_3 \xrightarrow{C_6H_6} Cp_2Zr(SC_6H_5)_2 + 2(CH_2CH_3)_3\ N{\cdot}HCl \qquad (17)$$

The sulfur and analogous selenium complexes are glassy solids, extremely air and moisture sensitive. The compounds are generally monomers when freshly prepared but in solution, or with aging in the solid state, polymerize with loss of solubility/14/.

Cyclopentadienyl zirconium complexes containing amido groups have also been reported. Reaction of tetrakis(dialkylamido)zirconium with a stoichiometric amount of cyclopentadiene yields the mono or biscyclopentadienyl derivative, Equation 18 /14/.

$$Zr(NR_2)_4 + xC_5H_6 \rightarrow [Cp_xZr(NR_2)_{4-x}] + (4-x)HNR_2 \qquad (18)$$

$x = 1, 2$

The amide derivatives can also be prepared via reaction between Cp_2ZrX_2 (X = Cl,Br) and a lithium or potassium amide. The physical and chemical properties of selected compounds are given in Table 6. Most of the compounds are air-sensitive and some are pyrophoric. The few Zr-N stretching bands which have been reported fall in the range 500-640 cm^{-1} (20-15 μm).

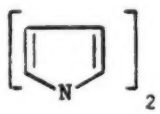
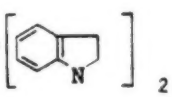
The nitrate derivative, $[CpZr(NO_3)_2]$, is prepared by the reaction of tetrakis(cyclopentadienyl)zirconium with nitric acid. The compound is benzene soluble and explodes on heating to 185°C /15/. The mononitrate, $Cp_2Zr(Cl)NO_3$, is more heat stable, mp 190.5°C. It is made from nitric acid and the dichloride. No ir data (νZr-N) are available.

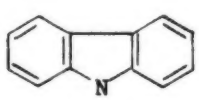
Zirconium forms elimination stabilized alkyls, ZrR_4, R = benzyl or allyl. The instablity of zirconium alkyl and aryl derivatives is due to facile decomposition by low activation energy pathways such as α and β elimination of zirconium hydride, homolysis, or coupling of ligands at the zirconium atom. The tetramethyl derivative, $Zr(CH_3)_4$, is unstable and decomposes at T < -15°C. The neopentyl derivative, $[Zr\{CH_2C(CH_3)_3\}_4]$, mp 103°C, in contrast to $[Zr(CH_3)_4]$ is a thermally stable tetraalkylated species. No ir data, νZr-C, are available.

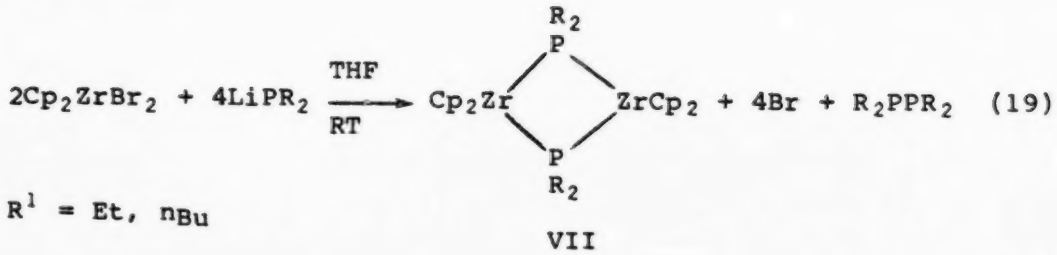
Few organometallic zirconium (III) compounds are known, no alkyl or aryl complexes have been reported. The only well-characterized Zr(III) complexes are the phosphido bridged dimers, VII, prepared as shown in Equation 19 /16/.

TABLE 6

SELECTED AMIDO COMPLEXES OF ZIRCONIUM/14/

Compound	Colour	Bp or Sublimation Temp (°C)	νZr-N cm^{-1} (μm)	Yield
$CpZr[N(CH_3)_2]_3$	yellow, slightly viscous liquid	94-96/0.05 mm	-	33
$Cp_2Zr[N(CH_3)_2]_2$	yellow, shining crystals	110-120/0.05 mm	-	54
$Cp_2Zr[N(C_2H_5)_2]_2$	orange-yellow solid	120-130/0.03 mm	-	64
$Cp_2Zr[N(C_4H_5)_2]_2$	orange crystals	mp 180	507 (19.7)	56
Cp_2Zr 	yellow-green	mp 195 (dec)	640 (15.6)	68
Cp_2Zr 	orange solid	mp 59-62	550 (18.2)	38
$Cp_2Zr(C_{12}H_8N)_2$*	orange-red solid	mp 216-219	530 (18.9)	31

*  = $C_{12}H_8N$



R^1 = Et, n_{Bu}

VII

Compound VII is thermally stable, not readily soluble, sublimes under high vacuum and is rapidly oxidized by air, I_2 and methyliodide.

The only Zr(II) complex known is a dicarbonyl derivative prepared as shown,

$$Cp_2ZrH_2 + CO \xrightarrow[50°C,\ 130\ atm]{C_6H_6} [Cp_2Zr(CO)_2]_n \quad \text{brown-black solid} \qquad (20)$$

The CO ir stretching frequencies occur at 1849 and 1945 cm^{-1} (5.4 and 5.1 μm, respectively).

A number of organozirconium complexes have been reviewed in this section. The majority of these compounds contain the unit Cp_2Zr. The synthesis of organometallic zirconium compounds requires a number of steps and yields are often low. Organometallic compounds which have an ir absorption within or close to the range of an ir laser, 9-16 μm (1111-625 cm^{-1}), include

- biscyclopentadienylzirconium alkoxides, $[Cp_2Zr(OR)_2]$, ν(Zr-O) bend 730 - 765 cm^{-1} (13.7 - 13.1 μm); and
- cyclopentadienyl(dialkylamido)zirconium complexes, $[Cp_xZr(NR_2)_{4-x}$, x=1,2], ν(Zr-N)500-640 cm^{-1}, 20 - 15 μm.

In the case of the amido complexes, it may be possible, with careful selection of the alkyl groups to shift the Zr-N stretch to a value within the range of the ir laser. The amido compounds are however air sensitive and some are pyrophoric, which may cause handling problems.

The compound $Cp_2Zr(H)BH_4$, ν(Zr-H)1945 cm^{-1}(5.1 μm), might in principle be a candidate for an ir laser isotope separation

process, but the Zr-H stretching vibration probably exhibits little isotopic discrimination since it is the relatively light hydrogen which vibrates and the heavy Zr scarcely moves.

Other candidates may be the β-diketonate derivates of Cp_2ZrCl_2. The zirconium-oxygen infrared stretching frequencies have not however been reported for the acac, hfacac or tfacac derivatives. These should be examined and the suitability of the compounds reassessed.

4.0 CONCLUSIONS AND RECOMMENDATIONS

The inorganic and organometallic chemistry of zirconium has been reviewed with the goal of identifying complexes which possess properties suitable for ir laser based zirconium isotope separation. The compounds identified as candidates, Sections 3.1 and 3.2, have Zr-ligand vibrations which occur very close to the outside edge of the range of an ir laser, 1111- 625 cm^{-1} (9 - 16 μm). With careful selection of the composition of the ligands surrounding the zirconium, ie those not directly associated with the Zr-ligand vibration to be irradiated, it may be possible to shift ν(Zr-ligand) farther into the practical range of an ir laser.

The candidate compounds are listed in Table 7. Of the compounds recommended for testing, those containing a Zr-O bond appear to be most promising. The extreme air sensitivity of the Zr-N containing species may necessitate more rigorous handling procedures than in the case of the Zr-O containing compounds.

Synthesis of a number of the candidate molecules requires many steps and product yields can be low, thereby making the compounds unattractive for industrial scale processes. All of the candidate molecules should however be tested, regardless of complexity and yields, in order to verify the ir laser isotope separation process. If the technique is viable, ways of improving product yields can be examined.

Candidate inorganic zirconium compounds outnumber organometallic species. Preparation of the inorganic compounds generally requires fewer steps than synthesis of organozirconium compounds. Organometallic compounds, specifically those containing the unit "Cp_2Zr", however, often have higher volatilities. This is an important property because the compounds must be in the gaseous state for irradiation.

An alternative to irradiating the Zr-ligand vibration may be to irradiate a bond whose vibration is influenced by the Zr atom, but does not directly involve Zr. To illustrate, irradiation of bond X-Y in the complex $[L_xZr\text{-}X\text{-}Y]$ instead of bond Zr-X. If

TABLE 7

SUMMARY OF CANDIDATE MOLECULES

Compound	R	Mp (°C)	Volatility (°C/mmHg)	IR Spectra ν(Zr-O) cm^{-1}	ν(Zr-O) (μm)	IR Spectra ν(Zr-N) cm^{-1}	ν(Zr-N) (μm)	Comments
$ZrOCl_2$(anh)				877	(11.5)			
$Zr(hfacac)_4$			N/A					
$Zr(tfacac)_4$		130-131	N/A					commercially available
$Zr(NR_2)_4$	Et	liq	110/0.01			557	(17.3)	commercially available
	n_{Pr}	liq	165/0.1			637	(15.7)	
	n_{Bu}	liq	180/0.1			637	(15.7)	
$Zr(O_2CR)_4$				650	(15.4)			thermally unstable
				470	(21.3)			
$Zr(SOCNR_2)_4$	Me			552-	(18-			
	Et			569	17.6)			
$Cp_2Zr(OR)_2$	C_6H_5			730-765	(~13) bend			
	Me			420-520	(24-17) stretch			
$Cp_2Zr(acac)Cl$				N/A				
$CpZr(hfacac)_3$				N/A				
$CpZr(tfacac)_3$				N/A				
$Cp_2Zr(NR_2)_2$		195 (dec)				640	(15.6)	

anh = anhydrous
N/A = not available

the influence of the Zr atom on bond X-Y is sufficient to achieve isotope separation, then the number of candidate complexes would increase considerably.

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